Atmos. Chem. Phys. Discuss., 11, C12252–C12255, 2011
www.atmos-chem-phys-discuss.net/11/C12252/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "From quantum chemical formation free energies to evaporation rates" *by* I. K. Ortega et al.

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Received and published: 23 November 2011

We would like to thank the referee for the useful comments which certainly helped us to improve the quality of the manuscript.

Answer to the referee comments:

"Namely, the authors should explicitly state that the conclusions made in this study are based on an approximate treatment of association rate by collision theory. This simpliïňĄed approach may greatly overestimate the association rate for clusters, leading to non-uniform (i.e., size- and structure-speciïňĄc) variations in the rate constant. Lower association rates would result in lower dissociation rates with non-uniform scaling between different clusters."

We agree with the referee when he/she says that association rates can differ from collision rates for a number of reasons. The main differences arise from activation energies, energy non-accommodation and steric hindrance.

When a cluster is formed in our system, covalent bonds are not broken (except for some proton transfers that occur more or less spontaneously when sufficient acids/bases are present). This fact, together with all our test calculations (energy calculations varying the molecular center of mass to simulate a collision), indicate that cluster formation does not have a kinetic barrier, and therefore is likely not an issue in our system.

The energy non-accommodation effect was already discussed in the text (page 27331, the paragraph starting in line 13). As stated in the text, in a previous work (Kurten et al. 2010) we have investigated the effect of energy non-accommodation in the formation of the sulfuric acid dimer. The conclusion of that work was that energy non-accommodation probably has a small effect in the case of sulfuric dimer formation, and that it will have an even smaller effect in larger clusters where more vibrational modes will be accessible for energy reallocation. So errors associated with not considering energy non-accomodation are likely small.

Regarding steric hindrance, sulfuric acid and ammonia are quite symmetric, "sticky" hydrogen-bonding functional groups pointing in all directions, so steric effects probably won't be an issue for collisions between them. Dimethylamine has two methyl groups which do not participate in hydrogen bonding, so in this case steric hindrance could have some effect, but again, considering the overall geometry of dimethyl amine, this factor is likely to be rather small.

For all these reasons, the relative uncertainty in the evaporation rates due to the uncertainties in the association rates is likely to be much smaller than that arising from the uncertainties in the free energies. In total, the uncertainty in the final evaporation rates is likely to be between 1 and 2 orders of magnitude. To clarify this fact in the manuscript we have added some more discussion about the possible sources of error

related to the use of collision rates as association rates:

"When two particles collide to form a larger cluster, they acquire an excess energy that needs to be dissipated. If this energy is not dissipated fast enough the cluster will break apart. In other words, if this energy non-accommodation is relevant, not all the collisions will lead to cluster formation events. Kurten et al (2010), however, showed that this is probably not a major effect in sulfuric acid clustering, and therefore we assume here that all collisions will lead to the formation of a cluster (i.e., the sticking factor is one). Energy non-accommodation is not the only factor affecting the sticking factor, as activation energies and steric hindrance can also be an issue. Since the cluster formation does not exhibit any kinetic barrier, it is very unlikely that activation energies have any effect in the present work. Steric hindrance can have some effect in the case of collisions with DMA molecule or DMA – containing clusters, since the molecule contains two methyl groups which do not participate in hydrogen bonding, but the effect of this on the overall sticking factor is likely to be small. In any case, the error associated with assuming a sticking factor of one will be smaller than the error associated with the calculation of formation free energies."

"1. Is there a point of including the data obtained by CBS-4M in the paper? This method, using uncorrelated HF for geometry and frequency calculations, is clearly inadequate for the task of cluster calculations."

We agree with the referee on this point; the CBS-4M method is not adequate for cluster calculations. On the other hand, a big fraction of ACP audience is probably not familiar with computational chemistry methods, so we think that including the data of CBS-4M in the manuscript illustrates how the choice of the computational method used in one's work is crucial. So, if the referee does not have a major concern about this, we would prefer to keep the CBS-4M results in the manuscript.

"2. It is not clear what does 'high level combination' refers to in line 24 on page 27336"

We agree with the referee also in this point. We have re-written the sentence as:

"The Gibbs free energy of formation of the sulfuric acid dimer calculated with the high level method combination (described in the supplementary material) is -7.91 kcal/mol (Table S.1.6)".

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 27327, 2011.